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EXAFS and XANES Study of Two Novel Pd Doped Sn/SnO_x Nanomaterials

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Abstract

EXAFS and XANES at the Pd and Sn K-edges have been used to characterise a novel palladium doped Sn/SnO_x nanocomposite that have found application in a new type of high performance solid-state gas sensor. The spherical nanoparticles (10 to 65 nm diameter) prepared either by co-decomposition of Sn and Pd organometallic precursors (doping in volume) or by decomposition of a palladium precursor on preformed Sn/SnO_x core-shell nanoparticles (doping in surface) consist of a tin metallic core surrounded by some small platelets of a well-crystallised material embedded in an outer layer of amorphous tin oxide. In this layer tin atoms in an oxidation state close to +IV, are four-fold coordinated to oxygen with bond distances slightly larger than in bulk cassiterite SnO_2. In both samples palladium was found to be always in a metallic state, only surrounded by Sn and Pd atoms located at unusually short distances. The two samples that differ mainly by their Pd coordination number present very different morphologies and electrical properties when fully oxidised. A possible location of the Pd atoms in these two materials is proposed.

1. Introduction

A new high performance gas sensor using the integrated circuit technology [1, 2] has been designed by depositing a drop of a suspension of a novel Sn/SnO_x nanocomposite [3, 4] doped with Pd onto a silicon die. This drop is then heated up to 600 °C using the integrated heater and a thin film of highly sensitive Pd doped nanostructured SnO_2 is generated onto the surface of the silicon wafer [2]. The suspension of monodisperse nanoparticles of Pd doped Sn/SnO_x [5] is prepared by a new chemical method based on the decomposition of Sn and Pd organometallic precursors in a controlled water/anisole mixture. Two different synthesis routes have been investigated: co-decomposition of Sn-based and Pd-based organometallic precursors (doping in volume) and decomposition of a palladium precursor on preformed Sn/SnO_x nanoparticles (doping in surface). A subsequent heat-treatment of these colloids carried out at 600 °C leads in all cases to Pd-doped SnO_2 nanoparticles that retain the same size and morphology. If the surface doping leads to a big improvement of the conducting properties of the oxidised sensor material, the volume doping produces a material that features poorer electrical properties than the undoped one. These contradictory results show that a detailed investigation of the structure and electronic properties of these nanocomposites is crucial to achieve a full understanding of the relationship between their structure and electrical properties. Mössbauer spectroscopy, XPS, HRTEM and X-ray diffraction have been already applied to characterise these colloids [4] but these techniques have shown some limitations due to the complex nature of these materials.

We report here an EXAFS and XANES study carried out both at the Sn and Pd K-edge of these two Pd doped Sn/SnO_x samples prepared by two different methods. The aim of this investigation is to complement the characterisation methods already used by a local order sensitive probe in order to better characterise the local structure and the electronic properties as well as to determine the dopant location in these colloids, precursors of the SnO_2-based sensor nanomaterials. This should allow for a better monitoring of the synthesis process that is essential to develop a reproducible low-cost synthetic method for large-scale production.

2. Experimental

2.1. *Preparation of the nanocomposites*

2.1.1. *Preparation of Pd doped in surface [Sn/SnO_x] colloidal suspension.* Preparation of the pure tin colloid from the $[Sn(NMe_2)_2]_2$ precursor in anisole containing traces of water follows the route described previously [3, 4]. The palladium precursor $[Pd(dba)_2]$ in anisol was added to a colloidal suspension of pure Sn/SnO_x ($[Pd]/[Sn] = 4\%$). After exposition to 1 bar of CO during 20 mn, depressurisation, decantation, filtration and drying under vacuum, a black powder was obtained and sampled by TEM.

2.1.2. *Preparation of Pd doped in volume [Sn/SnO_x] colloidal suspension.* The palladium precursor $Pd(OAc)_2$ was added to a solution of $[Sn(NMe_2)_2]_2$ in anisole containing traces of water in a Pd/Sn ratio of 8 wt%. The solution was then heated at 135 °C for 3 hours under magnetic stirring and a black suspension was obtained. After decantation the black precipitate was washed with anisole and sampled by TEM.

2.2. *Electron microscopy*

Samples for HRTEM studies were prepared in a glove box by slow evaporation of a drop of suitably diluted colloidal suspensions deposited on holey carbon-covered grids. The HRTEM experiments were performed at the "Service Commun de Microscopies de l'Université Paul Sabatier" on a JEOL JEM 2010 electron microscope working at 200 kV.

2.3. *X-ray Absorption Spectroscopy*

X-ray absorption data were collected on beamline 9.2 (CLRC Daresbury Laboratory, UK), operating under beam conditions of 2 GeV, 200 mA using a Si (220) double-crystal monochromator. XAS signals were measured in transmission mode at the Sn K-edge and in fluorescence mode using a 13-channel solid-state detector at the Pd K-edge. The spectra were recorded at 80 K by

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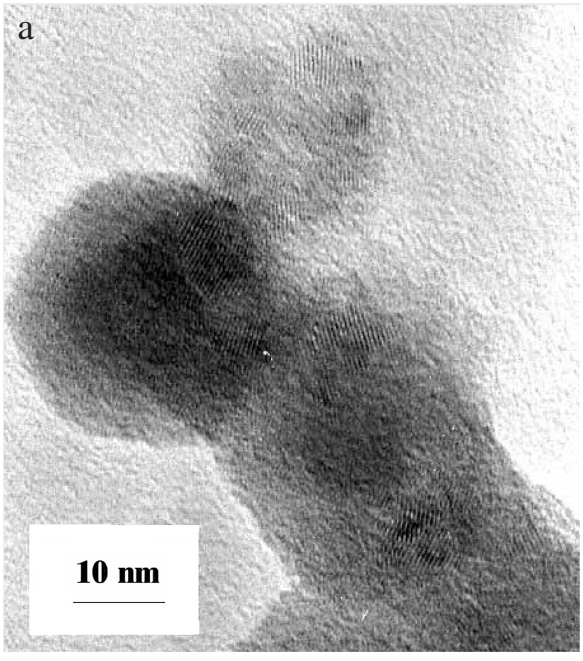
cooling the samples with a cold finger liquid-nitrogen cryostat. Appropriate amounts of sample were finely ground with boron nitride and pressed into 13 mm pellets producing a suitable edge jump. Data reduction of experimental X-ray absorption spectra was performed using the program EXBROOK [6]. EXAFS refinements with k^2 weighting were carried out with EXCURV98 [6] using Fourier filtering techniques with the same filter windows (0.8–4.0 Å).

3. Results and discussion

3.1. *Electron Microscopy*

Figure 1a shows the HRTEM image of a typical surface-doped nanoparticle in colloidal suspension that is clearly composed of a crystallised core of ca. 12 nm diameter surrounded by some small platelets of a well-crystallised phase embedded in an outer layer of amorphous material of ca. 4 nm thickness. XRD and Mössbauer results are consistent with the presence of an amorphous tin oxide surface layer surrounding a β crystallised tin core [4]. However, the coordination and oxidation state of tin in this layer as well as the exact nature of the platelets that are absent in the pure Sn/SnO_x material remain unclear. Figure 1b displays a HRTEM image of a typical volume-doped particle [5]. It is obvious that the particle size has increased dramatically to reach ca. 65 nm in diameter. As in the case of surface doped particles, the core of the particle appears to be surrounded by platelets of a rather crystalline material embedded in an outer amorphous layer.



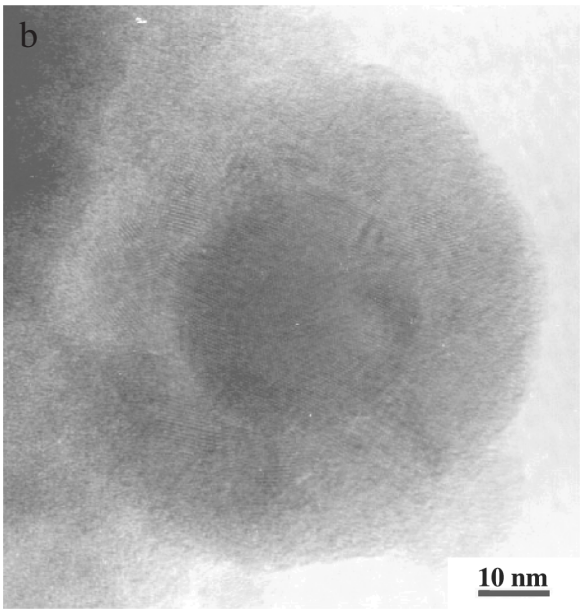


Fig. 1. HREM images of **a**: Pd surface-doped Sn/SnO_x nanoparticle; **b**: Pd volume-doped Sn/SnO_x nanoparticle.

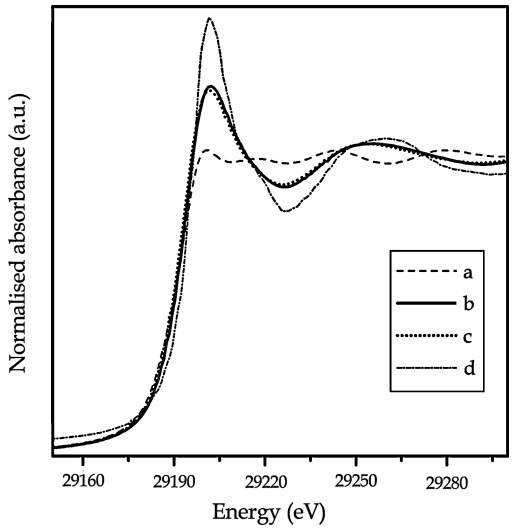


Fig. 2. Sn K-edge normalised XANES spectra of **a**: bulk Sn; **b**: Pd surface-doped Sn/SnO_x; **c**: Pd volume-doped Sn/SnO_x; **d**: bulk SnO_2.

3.2. *XANES*

3.2.1. *Sn K-edge.* Background corrected and normalised XANES of the two nanocomposites that are presented in Figure 2 along with Sn metal and bulk SnO_2 taken as references, show that the two nanomaterials have a very similar XANES profile. They both feature the white line characteristic of the oxide species but with a lower intensity than for the SnO_2 reference compound showing that the average oxidation state of Sn in this material is lower than in bulk SnO_2. Compared to SnO_2, the nanocomposites XANES spectra are also characterised by damped resonance peaks that usually shows the presence of a disordered phase and/or a large number of surface atoms. A mixture of an amorphous SnO_2 phase and a tin metallic phase is a possible explanation of the shape of this XANES profile.

3.2.2. *Pd K-edge.* Figure 3 shows the background corrected and normalised XANES of the two nanomaterials along with bulk PdO and bulk Pd presented as references. The two XANES spectra are almost identical and seem to have the same average electronic structure. The general profile of the spectrum of the Pd doped samples is similar to the one of bulk metallic Pd but with very much damped resonance peaks indicating the presence of disorder in the material and/or nanosize structures. The PdO spectrum has a totally different shape and its edge position is obviously shifted towards the higher energies as one might expect it for a higher oxidation state. The XANES analysis can already show that the Pd doped Sn/SnO_x samples are not oxidised and have an electronic

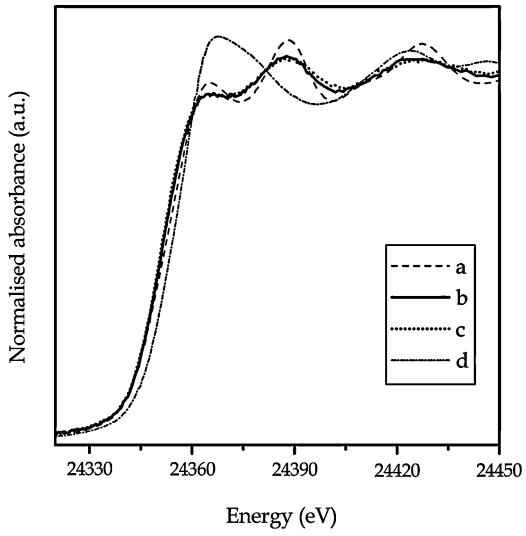


Fig. 3. Pd K-edge normalised XANES of **a**: bulk Pd; **b**: Pd surface-doped Sn/SnO$_x$; **c**: Pd volume-doped Sn/SnO$_x$; **d**: bulk PdO.

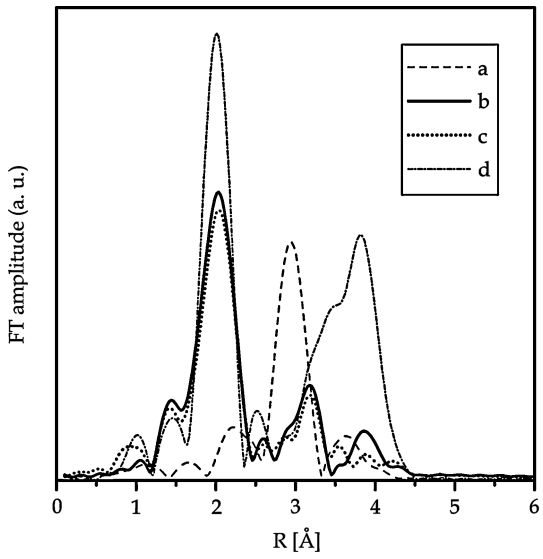


Fig. 4. Fourier Transforms of the k^3-weighted (references) or k^2-weighted Sn K-edge EXAFS of **a**: bulk Sn; **b**: Pd surface-doped Sn/SnO$_x$; **c**: Pd volume-doped Sn/SnO$_x$; **d**: bulk SnO$_2$.

Table I. *Summary of structural results of Sn and Pd K-edge EXAFS refinements of the two Pd-doped Sn/SnO$_x$ nano-materials.*

	Pd volume-doped Sn/SnO$_x$		Pd surface-doped Sn/SnO$_x$	
K-Edge	Sn	Pd	Sn	Pd
E_f (eV)	−8.5 (3)	−4.0 (8)	−6.8 (5)	−4.6 (4)
AFAC	1	0.80	1	0.80
k-range	2.5–15	3–14	2.5–15	3–14.5
N_1	3.3 (1) O	2.6 (5) Sn	3.3 (2) O	2.8 (4) Sn
R_1	2.071 (4)	2.55 (1)	2.073 (4)	2.58 (1)
A_1	0.010(1)	0.005(1)	0.008(1)	0.012 (1)
N_2	0.9 (3) Sn	0.5 (4) Pd	1.1 (4) Sn	2.3 (6) Pd
R_2	3.00 (1)	2.71 (4)	3.01 (1)	2.77 (1)
A_2	0.014 (5)	0.001 (2)	0.010 (4)	0.012 (3)
N_3	0.8 (3) Sn		1.9 (7) Sn	
R_3	3.25 (1)		3.27 (2)	
A_3	0.010 (4)		0.021 (8)	
N_4			0.6 (5) Sn	
R_4			3.75 (2)	
A_4			0.009 (8)	
N_5			0.1 (1) Pd	
R_5			2.58 (2)	
A_5			0.0006 (−)	
R (%)	15.1	16.4	18.6	14.3

E_f = contribution of the wave vector of the zero photoelectron relative to the origin of k [eV].
AFAC = amplitude reduction due to many-electron processes.
N_i = number of atom in the ith shell.
R_i = radial distance of atoms in the ith shell [Å].
A_i = Debye-Waller term of the ith shell ($A = 2\sigma^2$ with σ = Debye-Waller factor) [Å^2].
R factor in %.
*these parameters were kept fixed during the refinement.

structure close to the metallic state but with very small particle size and/or an amorphous character.

3.3. *EXAFS*

Results of the EXAFS structural refinements for the Sn and Pd K-edges measurements are summarised in Table I.

3.3.1. *Sn K-edge.* The phase corrected Fourier transforms (FT's) of the two Pd doped-samples are gathered in Figure 4. As the XANES data already showed, both nanocomposites feature a very similar FT. The first peak could be fitted for both samples with 3.3 O located at 2.071–2.073 Å from the central atom (Table I). This is similar to the values found for the undoped Sn/SnO$_x$ materials [7]. If we take into account the part of the Sn that belongs to the core of the colloid, the tin atoms in the oxidised phase are then likely to be 4 fold coordinated to oxygen [7]. The corresponding bond distances are only slightly larger than in bulk SnO$_2$ (2.045 Å) indicating that Sn has an oxidation state close to +IV. The second peak in the FT could be fitted with ca. 1 Sn atoms located at 3.00–3.010 Å from the Sn scatterer atom. This distance does not correspond to the Sn-Sn distance in SnO (3.515 Å) or SnO$_2$ (3.187 Å) tin oxides but to the bond distances in the tin metallic phase (3.022 Å) [8]. The relative amount of metallic tin atoms in the colloid was estimated using the Sn coordination number at ca. 25% [7]. The low intensity of the peaks beyond the metal tin shell show that the tin oxide phase is mainly in a disordered and/or amorphous state confirming the presence of a dispersed matter pointed out by HRTEM. The general fit of the surface-doped sample was slightly improved when a shell of ca. 0.1 Pd atoms located at 2.58 Å was added to the EXAFS model.

3.3.2. *Pd K-edge.* The Fourier transforms of the two nanomaterials presented in Figure 5 are different from one another. The results of the EXAFS refinement (Table I) show that the environment around the Pd atoms is composed for both samples of ca. 2.7 Sn atoms, located at a distance of 2.55 Å in the case of the volume-doped sample, and at a distance of 2.58 Å, consistent with the Sn K-edge fit results, in the surface-doped sample. These distances are shorter than tin-palladium bond lengths in alumina supported catalysts (ca. 2.63 Å) already reported by Choi *et al.* [9] and Pd-Sn distances in the Pd$_2$Sn phase (Pd-Sn 2.608 Å) [8]. Both samples feature a second shell of palladium atoms consisting of 2.3 atoms located at 2.77 Å for the surface-doped sample and of only 0.5 atoms located at 2.71 Å for the volume-doped sample. No other peaks could be detected indicating together with the XANES results that the Pd phase is rather amorphous and/or that this phase is composed of very small particles that are not oxidised but part of a metallic phase. The Pd-Pd distances found in these two samples (2.71–2.77 Å) are slightly different than the typical

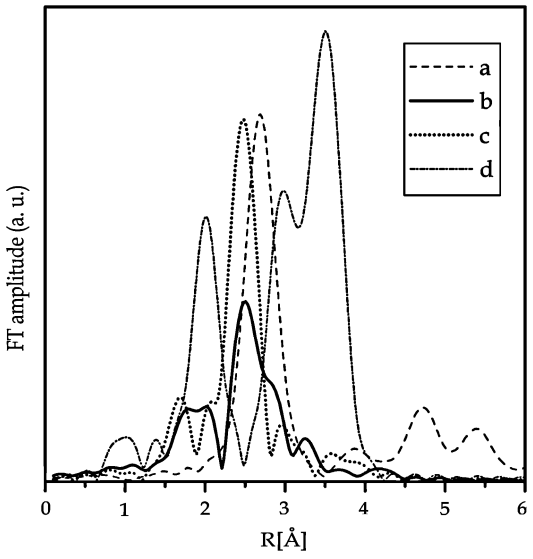


Fig. 5. Fourier Transforms of the k^3-weighted (references) or k^2-weighted Pd K-edge EXAFS of **a**: bulk Pd; **b**: Pd surface-doped Sn/SnO_x; **c**: Pd volume-doped Sn/SnO_x; **d**: bulk PdO.

bond distance of the palladium metallic phase (Pd-Pd 2.751 Å) [8]. The small discrepancy observed in the bond distances (ca. 1–2%) between the two samples may indicate that Pd atoms are in different locations and have different environments in each sample. The very low value of the Pd coordination number found for the volume-doped sample indicates that a better mixing of the Sn and Pd atoms occurs during the preparation process.

By combining the EXAFS results with the TEM images it is possible to propose two locations of the Pd dopant atoms in these nanomaterials. The first one is in small platelets of pure Pd surrounded by a tin/tin oxide interface located around the tin metallic core. These platelets were observed in both samples but mainly in the surface-doped one. The second location is in the Sn metallic core of the particle in which they form a bulk alloy with Sn and/or an Sn/Pd phase. A combination of these two locations seems to occur in the volume-doped sample.

Pd doped samples have been tested for their electrical properties after a full oxidation at 600 °C, in the working conditions of the gas sensor. The two Pd doped samples feature very different electrical properties. If the sample doped in surface shows an approximately 2-fold increase in its sensitivity to gases like CO compared to the undoped SnO_2 samples [10], the volume-doped sample features very poor electrical properties with a very high resistivity. The high amount of Pd (8 wt%) that has been used in this case as well as the different morphology could explain the dramatic change of the electrical properties in this sample.

4. Conclusion

The EXAFS and XANES results showed that the major part of tin in both Pd doped Sn/SnO_x nanocomposites is forming an amorphous oxide phase in which Sn atoms in an oxidation state close to +IV, are four-fold coordinated to oxygen atoms with an average bond distance slightly longer than in bulk cassiterite SnO_2. The presence of a metallic core estimated at ca. 25% of the total amount of tin atoms could also be pointed out. Pd is always in a metallic state and is surrounded by Sn and Pd atoms located at unusually short distances that vary according to the sample. A possible location of the palladium into the small crystalline platelets around the Sn core of the particle has been suggested for the sample doped in surface. For the sample doped in volume the formation both of a bulk Sn/Pd phase in the core part of the particle that could explain the huge increase in the particle size, together with the presence of Pd platelets around it has been suggested. When oxidised, the sample doped in surface features a large increased in its gas sensitivity compared to the pure one, whilst a very high resistivity have been measured in the sample doped in volume. This XAS study has allowed us in complement to the other techniques used, to fully characterise the structure of these materials by pointing out more specifically the location of the doping element in the two methods. These results should lead to significant improvement in the optimisation of the preparation method of these nanocomposites.

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